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(54) Removal method of glass adhered to sintered object during isostatic pressing process.

(57) Method of removing a layer of glass formed on a sintered body manufactured by hot isostatic pressing of a preformed body of inorganic powder such as silicon nitride powder, silicon carbide powder or the like with a pressure medium at a sintering temperature, wherein the sintered body of inorganic powder is retained in alkali solution at a high temperature for a predetermined time, preferably under a predetermined pressure.

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The present invention relates to a method of removing glass adhered to sintered objects of inorganic powder such as silicon nitride powder, silicon carbide powder or the like during hot isostatic pressing process.

In the manufacturing of sintered object of silicon nitride, a preformed body of silicon nitride powder coated with high-melting glass is subjected to hot isostatic pressing during which the preformed powder body is isotropically pressed with a pressure medium such as inert gas under pressure at a sintering temperature. The hot isostatic pressing is advantageous to manufacture sintered objects of complicated shapes having the same strength in all directions at a high sintering temperature. During the hot isostatic pressing process, however, the glass used as a sealing material is inevitably adhered to recesses of the sintered powder body. To remove the adhered glass from the sintered powder body, there have been proposed a hammering method of removing the glass from the sintered powder body by a mechanical external force applied thereto, a method of crystallizing the glass adhered to the sintered powder body under control of its cooling temperature after sintering to facilitate removal of the glass, and a method of removing the glass from the sintered powder body by vaporizing the pressure medium melted in the layer of glass for foaming the glass and cooling the foamed glass.

In the hammering method, it is required to mechanically apply a great external force to the sintered powder body for removal of the glass adhered thereto. This results in an increase of the manufacturing cost of this kind of sintered object. The second crystallizing method is effective only in use of special glass such as silica glass. In the third method, foaming of the glass is greatly influenced by a condition of the hot isostatic pressing and the kind of the glass. For the foregoing reasons, it is very difficult to remove the glass from the sintered powder body at a low cost.

It is, therefore, a primary object of the present invention to provide a method capable of easily removing the glass from the sintered powder body at a low cost.

According to the present invention, there is provided a method of removing a layer of glass formed on a sintered body manufactured by hot isostatic pressing of a preformed body of inorganic powder such as silicon nitride powder, silicon carbide powder or the like with a pressure medium at a sintering temperature, wherein the sintered body of inorganic powder is retained in alkali solution at a high temperature for a predetermined time.

Preferably, the removal method of glass is actually practiced as follows:

(1) To retain the sintered body in alkali solution stored in a closed container under a predetermined pressure.

(2) To use potassium hydroxide or sodium hydroxide as the alkali solution.

(3) To retain the sintered body in alkali solution at a temperature more than 100°C for more than one hour.

In addition, the removal method of glass may be adapted to a sintered body manufactured by hot isostatic pressing of a preformed body of ceramic powder or metallic powder. In the hot isostatic pressing, nitrogen gas may be used as the pressure medium.

With the removal method of glass described above, the glass adhered to the sintered body can be effectively removed in a condition where the sintered body is retained at a high temperature under presence of alkali solution. In this case, it is desirable that potassium hydroxide or sodium hydroxide is used as the alkali solution, and it is also desirable that the sintered body is retained in the closed container at a high temperature for more than one hour. Since in the removal method a brittle reaction layer is formed in the layer of glass adhered to the sintered body, the finishing time of the sintered body can be shortened.

Hereinafter, a preferred embodiment of the present invention will be described in detail. Prepared first in this embodiment were 3000-12000 preformed powder bodies each in the form of a silicon nitride ball of 13mm in diameter containing 93 percent by weight  $\text{Si}_3\text{N}_4$ , 4 percent by weight  $\text{Al}_2\text{O}_3$  and 3 percent by weight  $\text{Y}_2\text{O}_3$ . The preformed powder bodies were placed in a pot filled with borosilicate glass such as Pyrex glass containing 80.8 percent by weight  $\text{SiO}_2$ , 2.3 percent by weight  $\text{Al}_2\text{O}_3$ , 3.9 percent by weight  $\text{Na}_2\text{O}$  and 12.5 percent by weight  $\text{B}_2\text{O}_3$  the volume of which was approximately the same as the preformed powder bodies, and the pot was placed in a hot isostatic press device so that the preformed powder bodies are subjected to hot isostatic pressing at the sintering temperature of 1700°C under 700 atmospheric pressure. The preformed powder bodies thus sintered were cracked into blocks of about 4 cm in diameter, and the blocks were placed in a HU-100 type decomposition container made by Sanai Kagaku Kabushiki Kaisha. To remove the glass from the sintered powder bodies, alkali solution of 40 ml was added into the decomposition container at various concentration shown in an attached Table 1. In this test for removal of the glass, the pressure in the container was determined as shown in an attached Table 2 and calculated by Clapeyron-Clausius' equation.

In Table 1, double circle marks in the column of heating temperature and time each represent a condition where almost all the glass was removed from the sintered powder blocks, single circle marks each represent a condition where the sintered powder blocks were still covered with the glass which can be removed by the conventional hammering method, and "X" marks each represent a condition where the glass can not be removed from the sintered powder blocks.

As is understood from Table 1, it has been found that the glass adhered to the sintered powder body can be effectively removed in a condition where the sintered powder body is retained at a high temperature under presence of alkali solution. In this case, it is desirable that potassium hydroxide or sodium hydroxide is used as the alkali solution, and it is also desirable that the sintered powder body is retained in the decomposition container at a high temperature for a long time. With the test results represented by the double circle marks, it has been confirmed that a potassium hydroxide reaction layer of about 100 microns is formed in the layer of glass adhered to the sintered powder body. Since the potassium hydroxide reaction layer is brittle, the layer of glass adhered to the sintered powder body can be easily removed by abrasive processing. This is useful to shorten the finishing time of the sintered object.

In another embodiment of the present invention, sintered powder bodies each in the form of a SiC block of 5 x 5 x 10<sup>mm</sup> containing 98.5 percent by weight SiC, 0.8 percent by weight B<sub>4</sub>C and 0.5 percent by weight Free-carbon were manufactured by hot isostatic pressing in the same manner as described above and cracked into blocks of about 4 cm in diameter. The blocks of the sintered powder bodies were placed in the decomposition container used in the above embodiment. To remove the glass from the sintered powder bodies, alkali solution of 40 ml was added into the decomposition container at various concentration shown in an attached Table 3. In Table 3, double circle marks in the column of heating temperature and time each represent a condition where almost all the glass was removed from the sintered powder blocks, single circle marks each represent a condition where the sintered powder blocks were still covered with the glass which can be removed by the conventional hammering method, and "X" marks each represent a condition where the glass can not be removed from the sintered powder blocks.

Table I

|                        | AMOUNT OF<br>BLOCKS<br>(g) | CONCENT-<br>RATION<br>OF<br>REAGENT<br>(WT/V)% | AMOUNT OF<br>REAGENT<br>(ml) | Heating Temperature & Time |     |      |      |       |      |      |  |
|------------------------|----------------------------|--|------------------------------|----------------------------|-----|------|------|-------|------|------|--|
|                        |                            |  |                              | 160°C                      |     |      |      | 230°C |      |      |  |
|                        |                            |  |                              | 1hr                        | 5hr | 10hr | 16hr | 1hr   | 10hr | 16hr |  |
| Potassium<br>hydroxide | 30                         | 10   | 40                           | ×                          | ×   | ○    | ○    | ×     | ○    | ○    |  |
|                        | 30                         | 20   | 40                           | ×                          | ×   | ○    | ○    | ×     | ○    | ⊙    |  |
|                        | 30                         | 40   | 40                           | ×                          | ○   | ○    | ⊙    | ○     | ⊙    | ⊙    |  |
| Sodium<br>hydroxide    | 30                         | 10   | 40                           | ×                          | ○   | ○    | ○    | ○     | ○    | ○    |  |
|                        | 30                         | 20   | 40                           | ×                          | ○   | ○    | ○    | ○     | ○    | ⊙    |  |
|                        | 30                         | 40   | 40                           | ×                          | ○   | ○    | ⊙    | ○     | ⊙    | ⊙    |  |
| Lithium<br>hydroxide   | 30                         | 20   | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ○    |  |
|                        | 30                         | 40   | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ○    |  |
| Potassium<br>carbonate | 30                         | 40   | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ○    |  |
| Sodium<br>carbonate    | 30                         | 40   | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ○    |  |
| Hydrofluoric<br>acid   | 30                         | 10   | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ○    |  |
| Water                  | 30                         |  | 40                           | ×                          | ×   | ×    | ×    | ×     | ×    | ×    |  |

Table 2

| Reagent             | Temp. (°C) | Concentration (wt/v)% | Pressure (kg/cm <sup>2</sup> ) |
|---------------------|------------|-----------------------|--------------------------------|
| Potassium hydroxide | 160        | 22                    | 6.9                            |
|                     |            | 40                    | 5.7                            |
|                     | 230        | 22                    | 38.4                           |
|                     |            | 40                    | 32.2                           |
| Sodium hydroxide    | 160        | 20                    | 6.7                            |
|                     |            | 40                    | 5.1                            |
|                     | 230        | 20                    | 37.4                           |
|                     |            | 40                    | 30.7                           |

Table 3

|                     | AMOUNT OF BLOCKS (g) | CONCENTRATION OF REAGENT (WT/V)% | AMOUNT OF REAGENT (ml) | Heating Temperature & Time |     |      |      |       |      |      |  |  |
|---------------------|----------------------|----------------------------------|------------------------|----------------------------|-----|------|------|-------|------|------|--|--|
|                     |                      |                                  |                        | 160°C                      |     |      |      | 230°C |      |      |  |  |
|                     |                      |                                  |                        | 1hr                        | 5hr | 10hr | 16hr | 1hr   | 10hr | 16hr |  |  |
| Potassium hydroxide | 30                   | 10                               | 40                     | x                          | x   | ○    | ○    | x     | ○    | ○    |  |  |
|                     | 30                   | 20                               | 40                     | x                          | x   | ○    | ○    | x     | ○    | ●    |  |  |
|                     | 30                   | 40                               | 40                     | x                          | ○   | ○    | ●    | ○     | ●    | ●    |  |  |
| Sodium hydroxide    | 30                   | 10                               | 40                     | x                          | ○   | ○    | ○    | ○     | ○    | ○    |  |  |
|                     | 30                   | 20                               | 40                     | x                          | ○   | ○    | ○    | ○     | ○    | ○    |  |  |
|                     | 30                   | 40                               | 40                     | x                          | ○   | ○    | ●    | ○     | ●    | ●    |  |  |
| Lithium hydroxide   | 30                   | 20                               | 40                     | x                          | x   | x    | x    | x     | x    | ○    |  |  |
|                     | 30                   | 40                               | 40                     | x                          | x   | x    | x    | x     | x    | ○    |  |  |
| Potassium carbonate | 30                   | 40                               | 40                     | x                          | x   | x    | x    | x     | x    | ○    |  |  |

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**Claims**

- 5     **1.**   Method of removing a layer of glass formed on a sintered body manufactured by hot isostatic pressing of a preformed body of inorganic powder, ceramic powder or metallic powder having a glass covering using a pressure medium at a sintering temperature, wherein the sintered body of inorganic powder is retained in alkali solution at a high temperature.
- 10    **2.**   Method according to Claim 1, wherein the sintered body of inorganic powder is retained in alkali solution stored in a closed container under pressure.
- 3.**   Method according to Claim 1 or 2, wherein potassium hydroxide or sodium hydroxide is used as the alkali solution.
- 15    **4.**   Method according to any of claims 1 to 3, wherein the sintered body of inorganic powder is retained in alkali solution at a temperature more than 100°C for more than one hour.

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# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1932

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |  |  |
|---|--|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl.5)                |
| X   | EP-A-0 320 927 (ABB CERAMA AB)<br>* abstract; claims 1,9 *<br>* column 2, line 40 - column 4, line 41 *<br>* column 6, line 16 - column 7, line 42 *                   | 1-3  | C04B35/64<br>C04B35/56<br>C04B35/58<br>C04B41/91<br>B22F3/14 |
| Y   | ----   | 4  |  |
| Y   | WORLD PATENT INDEX LATEST, Derwent Publications Ltd., LONDON, GB, Week 8930.<br>&JP-A-1153579(Nagasaki Ken)15-06-1989<br>* abstract *                                  | 4  |  |
| X   | EP-A-0 118 702 (ASEA AB)<br>* abstract; claims 1,5 *<br>* page 2, line 30 - page 3, line 34 *<br>* page 4, line 16 - page 5, line 4 *<br>* page 8, line 23 - line 36 * | 1-3  |  |
| A   | GB-A-2 200 317 (AE PLC)<br>* abstract; claims 1-3,11 *<br>* page 2, line 26 - page 3, line 7 *<br>* page 4, line 3 - line 10 *<br>* page 5, line 5 - line 17 *         | 1-2,4  |  |
|   |  |  | TECHNICAL FIELDS SEARCHED (Int. Cl.5)                        |
|   |  |  | C04B   |
| The present search report has been drawn up for all claims  |  |  |  |
| Place of search<br>THE HAGUE  |  | Date of completion of the search<br>15 MAY 1992  | Examiner<br>OLSSON S. A.                                     |
| CATEGORY OF CITED DOCUMENTS   |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |
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